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Procedure for the separation of rhodium complex connections from aqueous solutions

The invention concerns a procedure for the separation in aqueous solution of contained catalytic of active rhodium complex connections on the one hand, from surplus available in the same solution, D.h. free complex ligands, their transformation and dismantling products as well as impurities on the other hand.

Rhodium complex connections are used together with surplus ligand in form of aqueous solutions as catalysts in different procedures.

In the DE-PS 26 27 354 a Hydroformylierungsverfahren is described, which uses such catalysts. It will be formed for water-soluble, organic Phosphin, which is present in the surplus, on the reaction conditions from rhodium, that in metallic form or begun as connection and. The water solubility of the Phosphin ligands is to be due to the presence of groups of sulfone acids in the molecule. The Phosphine is used preferentially in form of the alkali, ammonium or Erdalkalisulfonate. This procedure is characterised in particular by high selectivity regarding the education of geradkettiger aldehydes. Besides it avoids the emergence of larger quantities of high-boiling products.

In the course of the time to form very selectively geradkettige aldehydes with continuous function or with repeated employment the effectiveness of the catalyst system decreases the same catalyst solution. This selectivity loss has different causes. To them belong Katalysatorgifte like Eisencarbonyl, which form by effect of synthesis gas on the synthesis gas transportation lines or the construction material of the reactor, and high-simmering condensation products, which develop from the aldehydes. Selectivity-reducing also the reduction of the relationship from Phosphin works to rhodium, which amounts to in the again used catalyst 50 to 100 mole Phosphin per 1 g-atom rhodium. The change of the Phosphin rhodium relationship with longer application of the catalyst system is a consequence of dismantling and oxidation processes, the sulfonierten Phosphine is subjected to which. In the process of these reactions z become B. Phosphinoxide, Phosphinsulfide, aromatic sulfone acids and Disulfophenylphosphinsäure, in each case in form of their salts, in an educated manner.

Neither Phosphinoxide and Phosphinsulfide, nor the salts of aromatic sulfone acids and the Disulfophenylphosphinsäure are alone or together with rhodium catalytically we-came.

Is appropriate therefore, with fission products the loaded to replace aqueous catalyst solution occasionally altogether or partly by fresh solution. The used catalyst solution contains impurities, which are brought in with the reactants of water-soluble salts beside the above-mentioned transformation and dismantling products of the sulfonierten Phosphine rhodium as complex connection as well as surplus sulfoniertes Phosphin in form and frequently also. In order to secure the economy of the procedure, it is desired, both the rhodium complex and surplus to recover active Phosphin.

In the DE 32 35 029 A1 a procedure for the recuperation is described by catalyst systems, which contain water-soluble rhodium, sulfonierte organic Phosphine and cations. Here one adds first the existing groups of acids and at least equivalent quantity of acid to the aqueous solution of the catalyst system. Whereupon with an amine, which is solved in an organic solvent, and the separated organic phase, it is extracted contains the amine salt of the sulfonierten Phosphins, with the aqueous solution of an inorganic cousin, how NaOH mixes, intimately. Two phases, an aqueous, those form the Phosphinsulfonat and the rhodium complex connection contain and an organic, in which the amine is present. The aqueous Solution can be used directly or after dilution with water or after additive of sulfoniertem Phosphin again as catalyst solution.

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This procedure always supplies a mixture from the rhodium complex connection and the surplus ligand. A purposeful separation from rhodium complex connection and the other components is possible only in limited measure.

The DE-OS 19 12 380 concerns a procedure for the separation of co-ordination complexes of transition metals from a homogeneous fluid mixture of the complexes with one or more organic components using cellulose diaphragms. This function becomes and A. also to the separation of rhodium complex connections from mixtures uses, which contain the conversion products of the Hydroformylierung of low Olefinen in homogeneous phase. The rhodium complex connections are unsolvable in water, surplus ligands are not present not. The task of separation is limited to it, the mixture in the rhodium connection and the remaining components, in particular Olefine and aldehydes to divide.

In the case of processing aqueous solutions, which, result as catalyst used rhodium complex connections, surplus ligands, whose dismantling and conversion products and further, contain the selectivity of the catalyst reducing materials, problems, which do not arise to one or more organic components with the treatment of co-ordination complexes of the transition metals containing mixtures with. Thus their stabilizing effect on the rhodium complex is void by the separation of the ligands existing in the surplus. It is to be therefore expected that the complex connection breaks and is formed new rhodium complexes apart under inclusion by water, which is present in very large surplus. Alternatively only a fraction of the surplus ligands might be separated, in order to receive the original complex connection. Then however the danger exists that catalyst poisons and other one, possibly harmful working materials are removed only incompletely, and for rhodium complex connections are recovered, which can be reused only after additional cleaning steps as catalysts.

It existed to make therefore the task available a procedure, as large a separation as possible in aqueous solution more containing catalytically active rhodium complex connections on the one hand, of surplus available in the same solution, D.h. free complex ligands, whose transformation and dismantling products as well as further Verun permits to cleaning on the other hand. Precious metal losses are to be kept as small as possible.

This task solved by a procedure for the separation of rhodium complex connections, which contain water-soluble organic Phosphine as ligands from aqueous solutions, in which in addition surplus Phosphinligand and further components are solved if necessary. It is gekennzeichnet by the fact that one subjects the aqueous solution to a diaphragm separation process.

The new function is suitable in particular for the separation of rhodium complex connections from aqueous solutions, which are used as catalyst phase with the Hydroformylierung of Olefinen and for the re-establishment of their original selective effectiveness to be regenerated to have.

Surprisingly the procedure according to invention makes possible to separate the rhodium complex connection mostly available in small concentration from the remaining components the solution so selectively that they can be used without additional cleaning steps directly again as a component of the catalyst system. Arising rhodium losses are negligibly small.

It was not to be expected that only completely subordinated precious metal quantities are lost and that the rhodium complex connection the original activity and selective separated from the remaining components of the solution Effect maintains. Here it is to be considered that in the process of the processing process stabilizing conditions will leave the Komplexmolekül. To the effect of the high water surplus already one referred. The absence of strong complex ligands in the surplus should lead to a decay of the complex if necessary under separation of metallic rhodium.

Those the diaphragm separation process subjected solutions contain the rhodium Phosphinkomplex and beside water as main parts water-soluble organic Phosphine as well as their transformation and dismantling products. Among them organic remainders rank containing Phosphinoxide, Phosphinsulfide, sulfone acids, carbonic acids. Furthermore also Olefine, aldehydes, alcohols, Metallcarbonyl, in particular Eisencarbonyl, are hydrogen, to find Carbon monoxide and solution mediator in the solution if necessary according to their solubility in water.

The rhodium complex connections follow the general formula  $\text{HRh}(\text{CO})_x \text{L}^{4-x}$ , whereby L stands for the water-soluble Phosphinliganden and x means the numbers of 1 to 3.

As Phosphinliganden connections of the general formula  $\text{EMI}^9$  come.1 in consideration. Here  $\text{acre } 1 < , > \text{ acre } 2 < , >$  in each case < a phenyl > or a Naphthylgruppe, Y 1, Y < 2 >, Y < 3 > in each case < a geradkettige > or branched alkyl group with in each case 1 to 4 C-atoms, an alkoxy group with in each case 1 to 4 C-atoms, a halogen atom, which OH, CN, NO<sub>2</sub> or R 1 R 2 < N-group >, means < acre > 3, in which R < 1 > and R < 2 > for geradkettige or branched alkyl groups with in each case 1 to 4 C-atoms; X < 1 >, X < 2 >, X < 3 > is in each case a carboxylate (COO < - >) and/or sulfone RK (SO<sub>3</sub>) remainder, n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub> is resembles or different whole numbers from 0 to 5, M is an alkali metal ion, which or ammonium or quart acre a Alkylammoniumion of the general formula N (R 3 R 4 R 5 < R > 6 < >) stands < for equivalent > < of an alkaline earth metal > or < a zinc ion > in each case +, in < > R 3 < , > R 4 < , > R < 5 > R 6 for a geradkettige or branched alkyl group with 1 to 18 C-atoms. Worked satisfactorily in particular quaternäre groups of ammonium, in which R 5, R < 6 > 1 to < 4 > and < the fourth > remainder of 1 < to > 18 carbon atoms contains in each case three of the remainders of R 3, R 4. m < 1 >, m < 2 >, m < 3 > are resemble or different whole numbers from 0 to 3, whereby at least one number is < m > 1, < m > 2 or < m > 3 equal or larger than 1.

Solution mediators are materials or material mixtures, which are soluble at increased temperatures both in the aqueous and in the organic phase in particular. Their effect consists above all of changing the physical characteristics of the boundary surfaces between the two liquid phases and facilitating thus the transition of the organic reactants to the catalyst solution. Examples of these substances are salts of carbonic acids with 8 to 20 carbon atoms, Alkylsulfonate, quaternäre Oniumverbindungen, in particular ammonium salts, as well as adducts of the Ethylenoxids such as alkyl polyethylene glycols.

It is appropriate to filter before execution of the diaphragm separation process the aqueous solution around rough impurities, which can lead to a blockage of the diaphragm, to remove. Further it is favourably, before the separation also organic substances, above all such, which as solvents or source means for the diaphragm work, z.B. by extraction, distillation, Wasserdampfdestillation, to separate from the solution in order to exclude a damage of the diaphragm structure.

By the expression diaphragm separation processes are understood in particular the ultrafiltration and the hyperfiltration (written undertaking osmose, reverse osmose).

Ultrafiltration and hyperfiltration are selective molecular separation processes, with which the diaphragm works as molecular sieve. The diaphragm is able solved materials of sufficient molecule size at the diaphragm boundary surface restrainable, while smaller molecules pass the boundary surface, so that a separation the particles after its size takes place. The separation is caused by the fact that the large molecules are larger than the largest pores of the diaphragm, while the small molecules penetrate the diaphragm more or less unhindered. The separation processes are discussed, a recapitulatory description detailed in the literature are to z.B. in Ullmanns Encyklopädie of technical chemistry, 4. Edition (1978), Bd. 16, S. 515 FF.

After the function according to invention one supplies the aqueous solution of a side of the diaphragm under a pressure, which can be separated, which is larger than the pressure on the opposite side of the diaphragm. The difference of pressure must be larger thereby than the osmotic pressure of the system.

As diaphragm materials z have themselves.B. Cellulose, Celluloseacetat, PP, Polyimide, polyolefins, polyvinyl alcohols, Polyacrylnitrile, polysulfones and sulfonierte polysulfones work satisfactorily. Are particularly suitable Celluloseacetat, Polyimide, polysulfones and sulfonierte polysulfones. Celluloseacetat and polysulfones are preferred.

The diaphragms should be as thin as possible. It is demanded only that it the applied outside conditions of the separation process, in particular the pressure to withstand. Preferably one uses diaphragms, whose thickness amounts to 50 to 200 µm.

As high a life span of the diaphragms as possible is desired, in order to guarantee the economy of the procedure. Diaphragms from Celluloseacetat fulfill these conditions in particular. They hold back at least 98% of the rhodium complex connection with continuous function over more than 200 days, if 80% of the salts existing in the solution are separated as Permeat.

For the separation of the assigned substrate one works with flow-guiding devices, so-called modules. They have different for which respective application and know suitable shape, z.B. in the form of pipes, plates or spirals to be used. In the modules the diaphragms are arranged as flat or Schlauchfolien.

The conditions of work with the separation process according to invention depend substantially on the diaphragm and the composition of the solution, which is to be separated. The main variables of the procedure are the applied pressure as well as temperature and

concentration of the solution.

As already said, the pressure must be larger than the osmotic pressure of the system. It is affected further by the diaphragm material and the modular construction. Pressures from 0,6 to 6.0 MPa and from 1,2 to 2.0 MPa worked in particular.

The solution is preferably inserted into the separation process with a temperature from 10 to 80 DEG C, from 20 to 35 DEG C. It proved as appropriate that its salt concentration (D.h. the whole of all as salts available connections) 1.0 to 20 thread.- % preferably 3 to 16 thread.- %, and in particular 5 to 12 thread.- amounts to % (in each case related to the solution). Rhodium is to be present in the Lösung in a concentration from 10 to 1000 ppm, in particular 50 to 500 ppm.

There the solutions according to their use as catalyst usually 10 to 50 thread.- % salts and 100 to 2000 ppm rhodium (in each case related to the solution) contained, are to be adjusted the concentrations suitable for the separation if necessary by diluting the solution with entionisiertem water, which can be used.

Against the pH value of the solution which can be regenerated no special demands are made. Generally it is sufficient to preferably work within a pH range from 3 to 10, 4 to 9, and in particular 5 to 8. In the case of use of a cellulose acetate diaphragm it is advisable, pH values from 3,5 to 6, in particular from 4 to 5 to adjust.

The new procedure can be accomplished by paragraphs. In this case one separates the catalyst solution which can be regenerated from the remaining reaction participants, regenerates her according to invention and sets her for e neut.

Particularly it worked however to work continuously. With this procedure variant a portion of the catalyst solution is taken off continuously from the process, in which it is used, and subjected to the diaphragm separation process. The quantity of the taken off catalyst solution depends in particular on the extent of the dismantling and the transformation of the ligand. Of the diaphragm the held back, solution (Retentat), containing the rhodium complex connection, is again transmitted to the process, if necessary after additive of water-soluble organic Phosphin, in order to maintain the desired Rh/P relationship in the catalyst solution. In the solution, which passed the diaphragm (Permeat), is the conversion products of the complex ligands, the complex-forming organic Phosphinsulfonate and/or.- carboxylates, if necessary impurities as well as in traces rhodium. The Permeat is regenerated for the recuperation by rhodium and Phosphin. For this z is suitable. B., that as state of the art of far appreciative above procedures of the DE 32 35 029 A1.

In figure 1 an arrangement is represented for the intermittent execution of the procedure according to invention.

The one rhodium complex connection containing solution is supplied to a container 1 by way of a line 2. By additive of entionisiertem water over a line 8 the desired salt and rhodium concentration can be stopped. Over a line 3 the solution arrives at a pump 4 and on the necessary operating pressure is brought here. In a module 5, which contains the diaphragm, the separation of the solution takes place in Permeat and Retentat. The Permeat is supplied by way of a line 7 of the processing, the Retentat returns over a line 6 to the container 1.

Fig. the continuous arrangement of the new function points 2 to the recovery of an exhausted catalyst solution. The catalyst solution is supplied to 1, if necessary module 3 contained after dilution with entionisiertem water, which over a line 2 is fed, the diaphragm by way of a line. The Permeat is taken off over a line 4. A subset of the Retentats flows by a line 5 again to the module 3, another subset over a line 6 into the reactor is introduced.

In the following examples the procedure according to invention is more near described. The expression ?salt? is used for mixtures, which contain essentially the alkali salts of the Triphenylphosphin, Triphenylphosphinoxid and Triphenylphosphinsulfidmonosulfonsäure, - disulfonsäure and - tri sulfone acid and alkali salts of aromatic sulfone acids.

#### Example 1

The attempts A to g become in in Fig. 1 represented equipment accomplished. The separated Permeat is not transmitted however to a processing, but with the Retentat combines and into the container 1 led back. A goal of the attempts is the determination of the separative power of a diaphragm in the equilibrium with employment of same volumes of solutions of different concentrations and with application of different pressures.

The diaphragm used for the execution of the attempts (a product of the company Millipore, Handelsbezeichnung PCAC) consists of Celluloseacetat. It has a surface of 4,2 m < 2 > and as winding module is used. Their molecular Trenngrenze is 1000.

The aqueous solutions which can be regenerated contain 7.05, 8.90 and/or. 10.84 thread.- % salts and 88, 111 and/or. 136 ppm rhodium in each case related to the solution. They have a temperature from 27 to 30 DEG C. Per hour one transmits to the diaphragm 700 l solution.

The test conditions and the test results are arranged in table 1. EMI17.1

#### Example 2

In the equipment represented in figure 1 become from container 1 84 l (according to 88.5 kg) an aqueous solution, the 8.9 thread.- % Salz and ppm rhodium (in each case related to the solution), in a quantity of 660 l/h winding module contains 111 of a cellulose acetate diaphragm; Surface: 4.2 m < 2 >; a product of the companies Millipore) transmitted. The pressure amounts to 1.2 to 1.6 MPa, the temperature of the solution 30 DEG C. One receipt 18 to 25 l Permeat/h. The salt concentration in the Permeat amounts to 3 to 3.7 thread.- %, the rhodium concentration <1 ppm (in each case related to Permeatlösung).

The Retentat is driven in the circle and supplied to the diaphragm again; by addition from entionisiertem water the original salt concentration of 8,9 thread becomes in the Retentat.- % maintain.

If one continues the salt separation so far the fact that only 18% are contained of the salt quantity available in the initial solution in the Retentat is in the Retentat SIMILAR 640 ppm RH, in the Permeat SIMILAR 3 ppm RH.

In figure 3 the dependence of the rhodium concentration on the quantity of Retentat and in figure 4 the dependence of the rhodium concentration on the quantity of Permeat separated in each case is shown.

As follows from the course of the curve in the two diagrams, the diaphragm holds back than 98% of rhodium independently contained in the Retentat of the rhodium concentration in the Retentat always more.

The relationship RH to P (III) (in g-atom per mol) amounts to at the beginning of the separation procedure 1: and is to 39 because of the

end of the separation with 1: 7.

The preservation of the original activity and selective effect of the catalyst system by treatment in the procedure according to invention show the following example.

#### Example 3

In an agitating boiler, the 45 l aqueous catalyst solution (500 thread.- ppm RH, related to the solution; for each g-atom RH 80 mol of Triphenylphosphintrisulfonat) contains, becomes with 120 DEG C and a pressure of 5,0 MPa once per hour 5.5 kg propylene geleiten. One receives per to hour 8 kg of Butyraldehyd with a n/i relationship from 95: 5.

With increasing running time the P (III) is reduced: RH-relationship by formation of P (V) - connections with the consequence that debited to the n-aldehyde increased i-aldehyde is formed. Around the P (III): RH-relationship to keep constant, are extracted from the system for each day 1.5 to 3 l catalyst solution and separated according to the procedure according to invention over a diaphragm. One receives 5 to 10 l Retentatlösung. This solution - supplements around the portion of P (III), recovered from the Permeat - salts (0.1 - 0.15 kg/d) - one supplies to the reaction system again. The necessary water addition is reduced by the led back quantity of Retentat.

The reaction system can under the indicated conditions for months without activity and/or. Selectivity losses to be continuously operated.